

The Solid Phase Photolysis and Radiolysis of Ethylene at 20 to 77 K*

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Films of ethylene condensed onto a cold finger maintained at 20 K were irradiated with photons whose energy ranged from 8.4 to 21.2 eV. At the higher photon energies the relative yields of products compare well with those seen in the radiolysis of solid ethylene. Experiments on CH_2CD_2 demonstrate that in the photolysis hydrogen is mainly formed by the elimination processes $\text{CH}_2\text{CD}_2^* \rightarrow \text{H}_2(\text{D}_2) + \text{C}_2\text{D}_2(\text{C}_2\text{H}_2)$ and $\text{CH}_2\text{CD}_2^* \rightarrow \text{HD} + \text{C}_2\text{HD}$. The relative probabilities of these three processes are independent of the energy of the incident photons from 8.4 to 11.6 eV and are within experimental error identical to those observed in earlier gas phase photolysis experiments. Relative to acetylene, cyclobutane is a minor product at 8.4 eV but increases by an order of magnitude at higher energies where ions play a role. Cyclobutane, 1-butene and methylcyclopropane formed upon irradiation of frozen C_2H_4 – C_2D_4 mixtures consisted mainly of C_4D_8 , $\text{C}_4\text{D}_7\text{H}$, and C_4H_8 . Plausible mechanisms which may account for the formation of the latter products are examined. In the solid phase as in the gas phase the relative importance of H-atom production is seen to increase with increasing photon energy. Cyclopropane, apparently formed by insertion of CH_2 into C_2H_4 , is observed as a product at all wavelengths in the photolysis, and in the radiolysis.

Key words: Ethylene; free radical reactions; ion-molecule reactions; photolysis; polymerization; radiolysis.

1. Introduction

The condensed phase photolysis of simple olefins has not as yet been investigated in detail. Only one experiment dealing with ethylene (8.4 eV photons, 36 K) has been discussed [1]¹ in the literature. It was suggested that the products (1- C_4H_8 and methylcyclopropane) observed in the latter experiment were formed by the addition of ethylidene radicals to ethylene. The condensed phase radiolysis of olefins, on the other hand, has been investigated extensively [2, 3]. In the radiolysis studies on ethylene, 1-butene was noted as a major product and was thought to be produced by addition of an ethylene ion to ethylene. Hexenes, octenes, and decenes which were also observed were suggested to be formed by subsequent additions of product ions to ethylene. Isotopic analysis of the C_4 , C_6 , and C_8 products formed in the radiolysis of C_2H_4 – C_2D_4 did reveal [3c] that these products are indeed mainly formed by consecutive additions to form polymer molecules containing deuterium in multiples of four.

The purpose of the study reported here is to explore the processes occurring in the solid phase irradiation of ethylene more fully. The photolysis has been investigated at four different energies. At the lowest

of these energies (8.4 eV) ionic processes can be assumed to be relatively unimportant. At the highest energy (21.2 eV) it is likely that a large fraction of photons absorbed lead to the formation of ethylene parent ions. Therefore, this series of experiments may allow us to contrast the product formation which follows ionization with that associated with neutral excited molecule formation. In addition, certain aspects of the solid phase radiolysis have been re-investigated.

Finally deuterium labeling has been utilized in several experiments in order to examine in more detail the modes of formation of certain products.

2. Experimental Procedure

The apparatus and procedure for the solid phase photolysis and radiolysis experiments have been described previously [4, 5]. A detailed description of the rare gas resonance light sources has also been given in an earlier report [6]. The NBS 20,000 Curie cobalt-60 source was used for the gamma radiolysis experiments. One radiation experiment with 21.2 eV photons was carried out with a helium resonance lamp provided with an aluminum window [6]. Isotopic analyses of hydrocarbon products were carried out on a high resolution mass spectrometer using a low energy (12–15 eV) electron beam.

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¹ Figures in brackets indicate the literature references at the end of this paper.

3. Results

The relative yields of the major products which were measured are given in table 1. Only the sum of the hexene yields is given in the last column. At least eight different C_6H_{12} isomers are formed in the radiolysis as well as in the photolysis at all wavelengths. No attempt was made to analyze for products with molecular weights higher than those of the C_6 products. In the photolysis of $C_2H_4-C_2D_4$ mixtures at 11.6–11.8 eV, 70 percent of the hexene mixture consisted of C_6D_{12} , $C_6D_8H_4$, $C_6D_4H_8$, and C_6H_{12} .

Two products, cyclopropene and methyleyclopropene which were previously reported to be formed in the 8.4 eV photolysis of C_2H_4 at 36 K were not observed in our study. In accord with the observation made in the previous investigation, there was a compound which eluted from a squalane column between $i-C_4H_{10}$ and $1-C_4H_8$. However, mass spectrometric analysis indicated it to be a C_4H_4 isomer rather than methyleyclopropene (C_4H_6) as suggested previously. The yield of the C_4H_4 product was seen to increase relative to that of the other products when the irradiation time was increased. It may, therefore, be ascribed to secondary photolysis of a product, probably acetylene. Two other products, cyclobutene and an unknown C_4H_6 product were also seen to increase with the percent conversion of ethylene. At the lowest percent decomposition (0.02%), the yields of C_4H_4 and cyclobutene were less than 1 percent of that of acetylene. It is of interest that the cyclobutene product formed in the irradiation of a $C_2H_4-C_2D_4$ mixture with 8.4 eV photons consisted mainly ($\sim 90\%$) of C_4D_6 , $C_4D_4H_2$, $C_4D_2H_4$, and C_4H_6 . Such a distribution is consistent

with a mechanism involving the addition of an acetylene molecule to ethylene.

In pure ethylene, the relative yields of all products listed in table 1 showed only minor ($\sim 10\%$) variations when the percent conversion was varied over a 10-fold range (from 0.02 to 0.2%). The precision with which the relative yields are measured is approximately 10 percent for products whose yields are 1 percent or more of that of acetylene. For the other products the precision is estimated at 10 to 20 percent.

Quantum yields were not determined in any of the photolysis experiments. However, at any particular wavelength the yield of acetylene per unit time was seen to change by not more than 20 percent from one experiment to the next.

Besides the isotopic analyses referred to above and in tables 2, 3, and 4, several other products have been analyzed isotopically. Cyclopropane in the 11.6–11.8 eV photolysis of $C_2H_4-C_2D_4$ (1:1) at 20 K: C_3H_6-100 ; C_3DH_5-25 , $C_3D_2H_4-98$; $C_3D_3H_3-16$; $C_3D_4H_2-97$; C_3D_5H-11 and C_3D_6-89 . Cyclobutane in the 10.0 eV photolysis of $C_2H_4-C_2D_4$ (1:1) at 20 K: C_4H_8-120 ; C_4DH_9-6 ; $C_4D_3H_5-15$; $C_4D_4H_4-140$; $C_4D_5H_3-10$; $C_4D_6H_2-16$; C_4D_7H-11 , and C_4D_8-110 .

4. Discussion

Table 1 shows the relative yields of products formed in the photolysis of ethylene at 20 K with 8.4, 10.0, 11.6–11.8, and 21.2 eV photons, as well as in the gamma-radiolysis at 77 K. In the gas phase, the ionization energy of ethylene is 10.5 eV; [7] the ionization energy in the solid phase is unknown, and may be 1–2

TABLE 1. Products in the solid phase photolysis and radiolysis of C_2H_4

Radiation	Additive	C_2H_2	H_2	CH_3CHCH_2	$c-C_3H_6$	$c-C_4H_8$	$1-C_4H_8$	$2-C_4H_8$	$CH_3\cdot c-C_3H_5$	$n-C_4H_{10}$	C_6H_{12}
Relative yields											
Photolysis _b 8.4 eV	None	100	106	0.35	0.40	0.39	14.1	0.40	0.31	1.10	3.1
	Ar ^a	100	n.d.	0.22	0.12	0.47	13.5	0.25	0.20	0.82	n.d.
	O ₂ (5%)	100	110	0.42	0.40	0.50	11.0	n.d.	n.d.	0.38	n.d.
	CCl ₄ (6.3%)	100	n.d.	n.d.	0.13	0.39	10.1	0.25	n.d.	1.08	8.4
10.0 eV	None	100	90	1.4	1.1	3.05	16.0	1.15	0.63	1.90	16.9
	Ar ^a	100	n.d.	1.5	1.05	n.d.	20.7	1.20	0.60	2.07	n.d.
	CCl ₄ (6.3%)	100	n.d.	n.d.	0.49	3.40	20.0	0.40	n.d.	2.10	47.0
11.6–11.8 eV	None	100	n.d.	1.7	2.2	7.2	23.0	1.50	0.73	3.20	37.0
	CCl ₄ (6.3%)	100	n.d.	n.d.	0.55	7.3	29.0	1.40	n.d.	3.70	140.0
21.2 eV	None	100	n.d.	n.d.	n.d.	5.1	30.0	n.d.	n.d.	13.0	n.d.
Radiolysis ^c γ	None	100	n.d.	0.30	0.7	5.45	29.2	0.8	0.8	9.2	3.0
	CCl ₄ (6.3%)	100 ^d (1.4)	n.d.	n.d.	0.65	6.0	32.4	n.d.	1.1	9.9	6.0
		(1.5)									
	CCl ₄ (14.7%)	100	n.d.	n.d.	0.75	5.7	29.6	0.60	2.23	8.3	9.0
		(1.5)									

^aAr/ C_2H_4 = 50.

^bT = 20° K.

^cT = 77° K.

^dValues in parenthesis are G-values (molecules of acetylene formed per 100 eV).

TABLE 2. Hydrogen and acetylene from C₂H₄—C₂D₄ (1:1) at 20 K

	Percent distributions					
	C ₂ H ₂	C ₂ HD	C ₂ D ₂	H ₂	HD	D ₂
8.4 eV	59.0	7.0	34.0	61.0	3.0	36.0
11.6–11.8 eV	60.5	5.0	34.5	62.0	3.5	34.5
γ-ray	57.0	6.0	37.0	52.6	6.6	40.8

TABLE 3. Acetylene and hydrogen in the photolysis and radiolysis of CH₂CD₂

		C ₂ H ₂	C ₂ HD	C ₂ D ₂	D ₂	HD	H ₂
		Percent distribution					
Photolysis 8.4 eV	Gas	11.0	63.9	25.1	16.9	41.1	42.0
	Solid	23.1	37.3	39.6	23.9	38.0	40.1
10.0 eV	Gas	10.5	63.5	26.0	17.6	40.6	41.8
	Solid	21.7	41.7	36.6	20.6	39.1	39.6
11.6–11.8 eV	Gas	11.1	62.2	26.7	16.7	41.5	41.8
	Solid	14.1	53.4	32.5	16.8	41.0	42.2
Radiolysis γ	Gas	12.7	65.1	22.2	15.1	46.4	38.5
	Solid	17.7	52.7	29.6	26.5	31.0	42.5

Pressure in gas phase experiments: 10 torr.
Temperature in solid phase experiments: 20 K.

TABLE 4. 1-Butene yields from C₂H₄—C₂D₄ (1:1)

	γ-Rays 77 K	10 eV Photons 20 K	8.4 eV Photons 20 K
C ₄ H ₈	100	100	100
C ₄ H ₇ D	11	12	14
C ₄ H ₆ D ₂	5	7	11
C ₄ H ₅ D ₃	17	22	18
C ₄ H ₄ D ₄	122	125	110
C ₄ H ₃ D ₅	8	9	11
C ₄ H ₂ D ₆	3	4	5
C ₄ HD ₇	8	8	10
C ₄ D ₈	39	39	35

eV lower than the gas phase value [8]. Most likely, ionization is unimportant in the solid phase photolysis at 8.4 eV, which is more than 2 eV below the gas phase ionization energy, but in all other experiments shown in table 1, ionic processes undoubtedly play a major role. In the gas phase the photoionization quantum yield of C₂H₄ at pressures around 20 torr is approximately 0.2 and 0.9 at 11.6 and 16.8 eV respectively [6, 9]. The photoionization quantum yield of C₂H₄ in the solid phase is not known and may be expected to differ from the gas phase values. Keeping in mind the lack of knowledge concerning the ionization processes

in the solid phase, the modes of formation of some of the major products will now be discussed by considering both neutral and ionic mechanisms.

4.1. The Formation of Acetylene and Hydrogen

In the solid phase radiolysis and photolysis of ethylene, the major products formed at all energies are acetylene and hydrogen. It is seen, first of all, from the results obtained with C₂D₄:C₂H₄ (1:1) mixtures (table 2) that in the solid phase essentially all the hydrogen and acetylene are produced in molecular elimination processes or by geminate disproportionation reactions (which in such a mixture lead to the formation of C₂H₂ and C₂D₂, D₂, and H₂, exclusively). Although in the gas phase radiolysis C₂H₂ may be formed by charge transfer [10] from C₂H₂⁺ to C₂H₄ such a mechanism can be discounted in the condensed phase because of the reduced fragmentation of parent ions with increase in density [11]. Therefore, in the condensed phase photolysis and radiolysis, acetylene is tentatively assumed to be formed via decomposition of neutral excited ethylene molecules formed by direct excitation and by neutralization of the parent ion.

In the gas phase, the excited ethylene formed by absorption of 8.4 to 11.8 eV photons, dissociates as follows [9, 12]:

- (1) C₂H₄^{*} → CHCH + H₂
- (2) → CH₂C + H₂
- (3) → C₂H₂ + 2H

At atmospheric pressure the excited vinyl radicals formed as intermediates in process 3 dissociate at wavelengths below 147 nm (8.4 eV). Only at wavelengths above 155 nm, have stable CH₂CH radicals been noted [13]. In the condensed phase photolysis and radiolysis all, or at least a considerable fraction, of the vinyl radicals may be expected to be stabilized. Actually vinyl radicals have been observed by ESR in the liquid phase radiolysis of ethylene [3f].

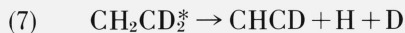
The occurrence of process 2 has been established from the isotopic distributions of the hydrogen products [12] formed in the photolysis of CD₂CH₂. The relative importance of processes 4 through 6 (i.e., 1 and 2) are approximately 0.41:0.42:0.17 in the gas phase, invariant with energy:

- (4) CD₂CH₂^{*} → CDCH + HD
- (5) → CD₂C + H₂
- (6) → CH₂C + D₂

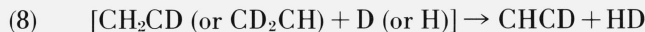
The gas phase results are compared with the analogous results obtained in the solid phase experiments in table 3. It is seen that the isotopic composition of the hydrogen fractions in the solid phase photolysis experiments closely resemble those observed in the gas phase.

Furthermore, in the solid phase photolysis experiments at 8.4 and 10.0 eV, there is a near equality between the yields of hydrogen and acetylene (table 1);

in fact, in the photolysis of CD_2CH_2 the yields of the various complementary isotopically labeled hydrogen and acetylene species match roughly ($\text{C}_2\text{H}_2 \approx \text{D}_2$, $\text{C}_2\text{HD} \approx \text{HD}$, $\text{C}_2\text{D}_2 \approx \text{H}_2$). This indicates that in these experiments, decomposition of vinyl radicals is indeed not important and that reaction 7, which in the gas phase accounts for a considerable fraction of the CHCD yield [12], occurs via an excited vinyl radical intermediate.

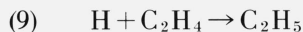


Assuming that in the solid phase experiments the disproportionation reaction



occurs with a low probability, it may be concluded that molecular hydrogen elimination processes occur via the same excited state in the gas as in the solid phase independent of the energy of the photon. In gas phase photolysis experiments the yield of acetylene is always considerably higher than that of "molecular" hydrogen ($\text{C}_2\text{H}_2/\text{H}_2 = 2.8$ at 10 eV). The occurrence of process 3 (process 7 in the case of CH_2CD_2) accounts for this, as is clearly illustrated by the fact that in all gas phase CH_2CD_2 experiments the abundance of CHCD in the acetylene fraction is considerably higher than that of HD in the hydrogen fraction. In the solid phase photolysis at 11.6–11.8 eV and in the radiolysis the abundance of C_2HD in the acetylene fraction is somewhat higher than that of HD in the hydrogen fraction indicating that at these energies reaction 7 may occur. Disproportionation reactions involving CH_2CD or CD_2CH and any other radical are however a more likely source of the excess C_2HD in the solid phase.

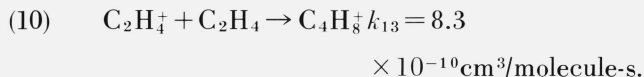
The absence of HD in the photolysis and radiolysis of $\text{C}_2\text{D}_4:\text{C}_2\text{H}_4$ (1:1) mixtures demonstrates that if H(D) atoms are indeed eliminated in the primary process they do not combine with other H atoms to form hydrogen in these experiments. The most probable fate of these H atoms especially if they are formed with excess kinetic energy, is addition to ethylene to form ethyl radicals:



The C_2H_5 radicals thus formed will combine or disproportionate with other radicals in situ or during warm-up. *n*-Butane is one of the products which may originate from such a free radical combination reaction. The fact that the yield of *n*-butane relative to that of acetylene is quenched by oxygen at 8.4 eV (table 1) supports this view. The relative yield of *n*-butane is seen to increase with the energy of the photon, indicating that the H-atom production becomes relatively more important at high energies. The highest yield of *n*-butane is observed in the 21.2 eV photon irradiation and in the radiolysis. Increasing H-atom production with increasing energy has also been noted in the gas phase photolysis of ethylene [9, 12], and is a general trend seen in the photolysis of other hydrocarbons [14].

4.2. The Formation of C_4H_8 Products

In the gas phase radiolysis of ethylene and in the photolysis at energies above the ionization energy, the ethylene parent ion reacts with ethylene to form C_4H_8^+ ions [15]:



In the presence of a charge acceptor (CA) such as $(\text{CH}_3)_2\text{NH}$ or NO, the C_4H_8^+ ions have been shown to react to form C_4H_8 products [16]



whose structures are assumed to correspond to the structures of the precursor C_4H_8^+ ions. In the gas phase at pressures of 100 torr or less, reaction sequence 10–11 leads to the formation of 2-butene and isobutene; the relative amounts of these isomeric C_4H_8 products depend on the energy in the C_4H_8^+ ion [17]. As the pressure is raised, for example, the formation of *iso*- C_4H_8 (i.e., *iso*- C_4H_8^+) is quenched. If reaction 10 can compete with neutralization of the C_2H_4^+ ions in the solid phase, it is possible that the resulting C_4H_8^+ ions might lead to the formation of C_4H_8 products, through neutralization of the ion:



It has actually been suggested before [3c] that in the solid phase radiolysis reaction 10 followed by 12 might account for the formation of 1-butene.

The results given in table 1 show that 1-butene is the most important C_4H_8 product in all the solid phase experiments. More than 80 percent of the 1-butene formed in the photolysis and radiolysis of $\text{C}_2\text{D}_4\text{—C}_2\text{H}_4$ (1 : 1) mixtures (table 4) consists of C_4H_8 , $\text{C}_4\text{H}_4\text{D}_4$, and C_4D_8 . That is, 1-butene seems to be formed mainly by the combination of two $\text{C}_2\text{H}_4(\text{C}_2\text{D}_4)$ units.

As mentioned above, in the gas phase very little 1-butene is formed in reaction sequence 10–11; isomerization of the C_4H_8^+ ions formed in reaction 10 to the 1- C_4H_8^+ structure is evidently an improbable process under those conditions. The fact that the yield of 1-butene is relatively large in the 8.4 eV photolysis where ionization is presumably unimportant, and furthermore undergoes a relatively small increase with increasing energy, seems to indicate that the 1-butene is at least in part formed through a nonionic mechanism. A plausible mechanism which would lead to the observed isotopic distribution in the $\text{C}_2\text{H}_4\text{—C}_2\text{D}_4$ (1 : 1) experiment would be H atom elimination from ethylene and addition of the hot H-atom to a neighboring ethylene molecule (reaction 9), followed by a recombination in the cage of the two radicals (reaction 13).

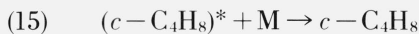


It is of interest that the increase in the yield of 1-butene with photon energy parallels the increase in the yield of *n*-butane, which as we have shown above, is formed in a reaction sequence involving H atom addition to ethylene. The presence of deuterium labeled butenes other than C₄D₈ and C₄D₄H₄ in the photolysis and radiolysis of C₂H₄–C₂D₄ mixtures might be explained by the participation of diffusive recombination of vinyl and ethyl radicals in the overall 1-butene production. Increased diffusion would explain the observation that butenes such as C₄H₇D, C₄D₇H, CH₃D₅, and C₃H₅D₃ are formed at relatively higher yields in the liquid phase [3d] than in the solid phase radiolysis and that in the liquid phase they increase relative to the yields of C₄H₈, C₄H₄D₄ and C₄D₈, with an increase in temperature [3d].

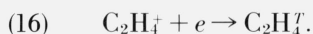
It is understood that proposed mechanism is a tentative one and that other mechanisms such as those proposed in previous studies cannot be ruled out.

Of the C₄H₈ products formed in the solid phase irradiations of ethylene (table 1) there is one product, cyclobutane, which seems to be formed via a C₂H₄⁺ intermediate. This statement is based on the fact that the relative yield of cyclobutane is very small in the photolysis with 8.4 eV photons where presumably few ions are formed (cyclobutane was not even detected in the earlier study [1] at this energy), and increases by nearly an order of magnitude when the photon energy is raised to 10.0 eV and again increases when the energy is raised to 11.6–11.8 eV. This large increase in yield with energy can be contrasted with the yields of the butene products, which increase by less than a factor of two when the energy is augmented from 8.4 eV to 11.6–11.8 eV. Furthermore, the fact that approximately 90 percent of the cyclobutane formed in the photolysis and radiolysis of C₂D₄–C₂H₄ mixtures consists of C₄H₈, C₄H₄D₄, and C₄D₈ (see Results) indicates that this product is formed mainly in a reaction of C₂H₄ (C₂D₄) entities as has been shown before [3d] in the liquid phase radiolysis of ethylene.

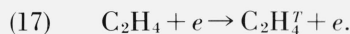
Cyclobutane is also formed in the mercury photosensitized photolysis [18] of ethylene at a pressure of 700 torr, with a quantum yield of 3.8×10^{-6} . In those experiments, the cyclobutane product was suggested to be formed as a result of a reaction between triplet state ethylene and ground state ethylene:



If, in the solid phase photolysis experiments, cyclobutane originates in reaction 14 we must conclude that the formation of triplet state ethylene is important only at photon energies higher than 8.4 eV. This could be explained if triplet state ethylene were formed in a neutralization reaction such as:



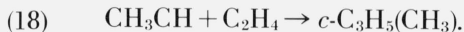
In radiolysis, triplet ethylene may also be formed by direct excitation:



Cyclobutane has been reported [19] as a product (*G* ~ 0.1) in the gas phase radiolysis of C₂H₄ (pressure: 100 torr) and ascribed to the participation of triplet ethylene. Reaction 17 cannot be operative in the 10 and 11.6 eV photolysis experiments, since the ejected electrons will have insufficient energy to bring about the optically forbidden transition to the lowest triplet state at 3.6 eV [20].

The 2-butenes are formed as minor products in all the solid phase irradiations given in table 1. Their yield shows little or no variation with increasing energy; hence, their formation is probably not associated with an ionic process. This is of interest, since, as indicated above, in the gas phase at pressures of 100 torr or less, it has been shown that reaction 10 of the ethylene ion with ethylene leads mainly to the formation of 2-C₄H₈⁺ ions. Thus, at any rate, the absence of 2-butene as an important product in any of the solid phase experiments demonstrates that C₄H₈⁺ ions formed in reaction 10 do not undergo neutralization to form 2-C₄H₈, under these conditions.

Methylcyclopropane is also formed in small yields in all the solid phase photolysis and radiolysis experiments reported in table 1. In experiments carried out with C₂H₄:C₂D₄(1:1) mixtures, about 75–80 percent of this product consists of C₄H₈, C₄H₄D₄, or C₄D₈. In an earlier study [1] of the solid phase photolysis of ethylene at 8.4 eV, the formation of methylcyclopropane was attributed to a reaction of an ethylidene with ethylene:



Although this mechanism which requires a rearrangement of a long-lived excited ethylene molecule would indeed account for the isotopic distribution of methylcyclopropane products formed in the C₂H₄:C₂D₄ mixture, a free radical mechanism occurring in the cage may also explain the experimental observation. Addition of CH₂CH to C₂H₄ occurs with a low activation energy (0.14 eV) for thermal CH₂CH radicals and may involve a neighboring molecule, especially if, as in the gas phase, the CH₂CH retains some internal energy after its formation. Such an addition process would lead to the formation of the 3-butenyl radical [3f] and conceivably also of the methylene cyclopropyl radical. These two radicals may capture a neighboring hydrogen atom to form dimeric 1-butene and methylcyclopropane respectively.

4.3 The Formation of Cyclopropane

The results given in table 1 show that cyclopropane is a product in all experiments. Since the addition of methylene to ethylene to form cyclopropane:



is a well-known reaction [21], the presence of this product suggests that methylene is formed in the solid

phase photolysis and radiolysis of ethylene. Indeed, the isotopic composition of the cyclopropane produced in the photolysis and radiolysis of a $C_2H_4:C_2D_4$ (1:1) mixture (see Results) indicates that more than 80 percent of the cyclopropane consists of $c\text{-}C_3H_6$, $c\text{-}C_3H_4D_2$, $c\text{-}C_3D_4H_2$, and $c\text{-}C_3D_6$. This distribution is consistent with the formation of cyclopropane through addition of $CH_2(CD_2)$ to $C_2H_4(C_2D_4)$. Insertion of a CH_2 species into a $C-H$ bond of ethylene would also lead to the formation of propylene



Propylene is formed as a product in these experiments (table 1), but has not been analyzed isotopically.

If indeed the cyclopropane and propylene products can be assumed to result from reactions 19 and 20, we can infer the occurrence of the primary process:



This process requires less than 8.3 eV [7a] so there is enough energy available even in the 8.4 eV photolysis for its occurrence. It is seen that in the photolysis the relative importance of cyclopropane formation increases with increasing energy.

4.4. The Formation of Hexenes

Several C_6H_{12} products are formed in the solid phase irradiations. The total yields of these products are listed in table 1.

The yields of the hexene products are relatively small in the 8.4 eV photolysis, but undergo a large increase when the energy is raised to 10.0 eV, and more than double again when the energy is further raised to 11.6–11.8 eV. These observations are very similar to those made above concerning the yields of the cyclobutane product. As in that case, we can infer that the large increase in yield when the energy is raised to a point where ionization is certainly of importance (10.0 eV) may be related to participation of ions in the formation of the products in question. It has been reported before [3c] that the 2-hexene product formed in the radiolysis of a $C_2D_4-C_2H_4$ (1:1) mixture at 77 K consisted of more than 75 percent C_6H_{12} , $C_6H_4D_8$, $C_6H_8D_4$, and C_6D_{12} . In the present study (see Results) it is seen that the 2-hexenes, as well as the 1-hexene product have a similar isotopic composition when an equimolar ethylene mixture is irradiated with 11.6–11.8 eV photons. That is, most of the hexene products are evidently made up of $C_2H_4(C_2D_4)$ units.

In the earlier radiolysis study [3c] it was suggested that hexene is formed in a process initiated by reaction of the $C_2H_4^+$ ion with ethylene and terminated by electron recombination with a $C_6H_{12}^+$ species. The present

photolysis experiments seem to substantiate this interpretation. Especially if one considers that an electron scavenger such as CCl_4 has a profound effect on the yields of the hexene (table 1). The actual role of CCl_4 in the enhancement is uncertain. It is however of interest to note that the yields of the C_4 products are not seriously affected by CCl_4 .

5. References

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